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Abstract. The crystal structure, magnetic and magnetothermal properties of non-stoichiometric $TbCo_2Mn_x$ and $TbCo_2Ni_x$ alloys were studied. It was shown that single-phase compounds with the $MgCu_2$-type structure exist up to a certain content of x (x <0.4 for compounds with Mn and $x \leq 0.1$ for compounds with Ni). The concentration changes of the lattice parameter, Curie temperature, magnetic moment of the 3d sublattice in $TbCo_2Mn_x$ and $TbCo_2Ni_x$ alloys were compared. The magnetocaloric effect in alloys were estimated using data of magnetic and heat capacity measurements.

1. Introduction

Recently, new non-stoichiometric RM_2Mn_x compounds (R - rare-earth metal, M - 3d transition metal Ni, Co) are revealed and their physical properties are actively investigated [1-7]. These compounds crystallize in the $MgCu_2$-type structure (cubic Laves phase C15, space group $Fd\bar{3}m$) same as the binary RM_2 compounds. Part of the Mn atoms occupy the 3d metal positions (16d), the remaining part occupies the rare-earth element positions (8a). It is noteworthy that the Curie temperature (T_C) of the RM_2Mn_x compounds may be significantly higher than T_C of the RCo_2 and RNi_2 parent compounds.

The practical interest in studying the magnetic properties of nonstoichiometric RM_2Mn_x compounds is partially related with the intensive search for materials with large magnetocaloric effect. For example, it was shown, that the maximum of the magnetocaloric effect is persisting in very wide temperature range for $GdNi_2Mn_x$ and $ErCo_2Mn_x$ [4, 5]. This allows considering non-stoichiometric compounds as possible candidates for magnetothermal applications.

On the over hand, rare-earth intermetallic compounds with cobalt, which have the $MgCu_2$-type structure, are simple model objects for the study of band metamagnetism. The magnetic state of the cobalt sublattice can be changed either due to the influence of the molecular field of the rare earth sublattice in compounds with magnetic R, or due to a change in the electronic band structure in compounds in which cobalt is partially replaced by various elements (Al, Ga, Mn, Si, Cr, Ni and etc.) [8-10].

In this paper, we study the influence of manganese and nickel on the formation of non-stoichiometric $TbCo_2M_x$-type compounds (M = Mn, Ni) with the $MgCu_2$ type structure and the formation of their physical properties. The changes in the crystal lattice parameter, Curie temperature, magnetic moment of the 3d sublattice, and magnetocaloric effect on the concentration of Mn and Ni in $TbCo_2M_x$ are compared.

2. Experimental details

The ingots of the $TbCo_2Mn_x$ and $TbCo_2Ni_x$ alloys were prepared by induction melting of the constituents in alumina crucibles in argon atmosphere. In order to obtain the equilibrium phase state, the ingots were annealed at 800°C for 7 days. Structural and magnetic studies were performed at the Centre of Collective Use of the Institute of Metal Physics UB RAS. Room temperature X-ray diffraction patterns were measured for powdered samples with the average particle size 30–50 μm using an Empyrean (PANalytical) diffractometer with Cu Kα radiation. The x-ray diffraction patterns were analysed with the High-Score v.4.x software.

Magnetic measurements were carried out using spherical samples. The magnetization in high magnetic fields of to 10 T was measured in a temperature range of 4.2–320 K by pulsed technique using a pulse magnetometer and a magnetic field pulse duration of 8 ms. The heat capacity was measured using the low-temperature adiabatic calorimeter.

3. Results and discussion

The non-stoichiometric $TbCo_2Mn_x$ and $TbCo_2Ni_x$ compounds crystallize into the cubic $MgCu_2$ type structure at a certain concentration x (x <0.4 for compounds with Mn and $x \leq 0.1$ for compounds with Ni) [11, 12]. The formation of non-stoichiometric $TbCo_2M_x$ compounds with the $MgCu_2$-type structure apparently occurs as in the case of the previously studied non-stoichiometric compounds, due to the fact that the M atoms occupy the positions of both the rare-earth element (8a) and cobalt (16d).

For compounds with nickel, the concentration interval for the formation of compounds with the $MgCu_2$ structure is less than with manganese. This may be due to the fact that for the formation of non-stoichiometric $TbCo_2M_x$ the atomic radius of the M metal should be closer to the atomic radius of terbium (r_{Tb} = 0.1773 nm). Consequently, Mn is most appropriate metal for formation of such type compounds because its has the largest atomic radius among 3d transition metals Co (r_{Co} = 0.125 nm),

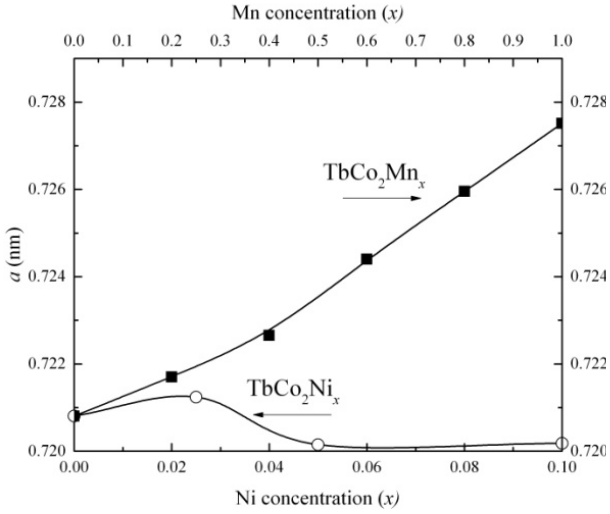

Figure 1. Concentration dependences of the lattice parameter for non-stoichiometric $TbCo_2Mn_x$ (■) and $TbCo_2Ni_x$ (○) alloys.

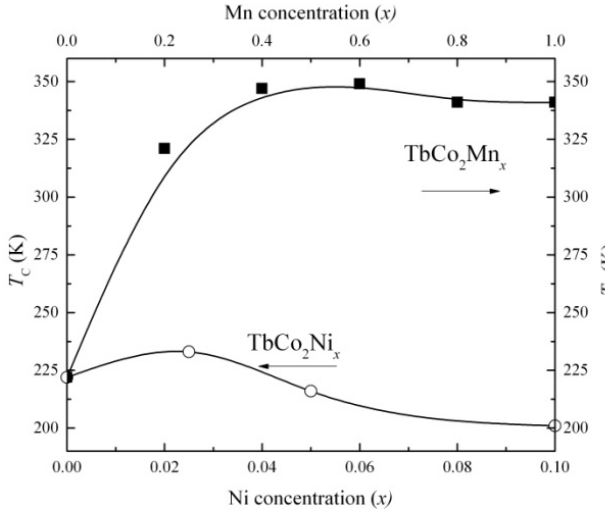

Figure 2. Concentration dependences of the Curie temperature for non-stoichiometric $TbCo_2Mn_x$ (■) and $TbCo_2Ni_x$ (○) alloys.

Ni (r_{Ni} = 0.125 nm), and Mn (r_{Mn} = 0.137 nm).

Figure 1 shows the concentration dependences of the lattice parameter of non-stoichiometric $TbCo_2M_x$ alloys. It can be seen that for compounds with manganese, the lattice parameter monotonically increases with increasing manganese content. At the same time, for compounds with nickel, a nonmonotonic change in the lattice parameter is observed.

With the addition of Mn, the Curie temperature of $TbCo_2Mn_x$ sharply increases and reaches a maximum value of 350 K at a manganese concentration of x = 0.4 (figure 2). Qualitatively, the concentration dependence of T_C for $TbCo_2Mn_x$ is similar to that observed in substitutional

$R(Co_{1-x}Mn_x)_2$ solid solutions [8]. In particular, in $R(Co_{1-x}Mn_x)_2$, the dependence $T_C(x)$ sharply increases

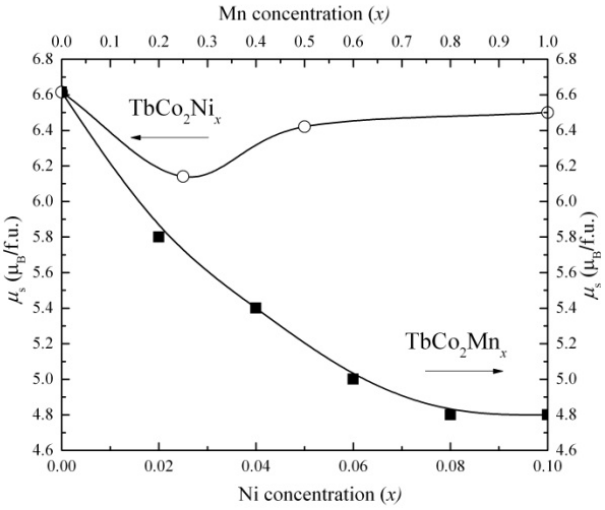

Figure 3. Concentration dependences of the spontaneous magnetic moment μ_s at 4 K for non-stoichiometric $TbCo_2Mn_x$ (■) and $TbCo_2Ni_x$ (○) alloys.

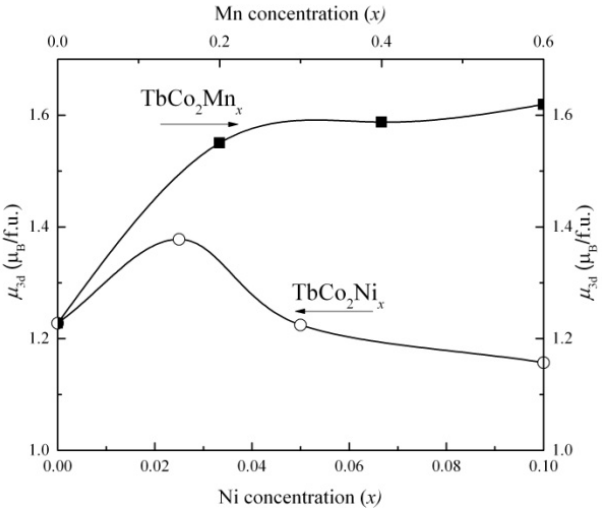

Figure 4. Concentration dependences of the magnetic moment of 3d-sublattice μ_{3d} for non-stoichiometric $TbCo_2Mn_x$ (■) and $TbCo_2Ni_x$ (○) alloys.

with increasing x and decreases with a further increase in x.

For $TbCo_2Ni_x$, when Ni is added T_C increases at small x, and then decreases (figure 2). The shape of $T_C(x)$ dependence is similar to the concentration dependence of T_C in substitutional $R(Co_{1-x}Al_x)_2$ solid solutions with nonmagnetic Al [10].

Figure 3 shows concentration dependences of the total spontaneous magnetic moment of the compounds μ_s which was determined using the magnetization curves $M(H)$ measured in fields up to 10 T at temperature of 4.2 K [11, 12]. It can be seen that for $TbCo_2Mn_x$, μ_s decreases monotonically with increasing of x because the magnetic moment of the 3d sublattice is oriented antiparallel to the magnetic moment Tb. In the case of nickel, the spontaneous magnetic moment changes nonmonotonic.

Figure 4 shows the concentration dependence of the magnetic moment of the 3d sublattice (μ_{3d}). μ_{3d} was calculated under the assumption that the magnetic moments Tb and 3d are oriented antiparallel as:

$$\mu_{3d} = (\mu_{Tb} - \mu_s)/(2 + x). \quad (1)$$

Here we assume terbium magnetic moment to be equal to its free-ion value $\mu_{Tb} = 9\ \mu_B$, which was confirmed for $TbCo_2$ by neutron diffraction experiments [13].

The concentration dependences of the magnetic moment of the 3d sublattice $\mu_{3d}(x)$ for compounds with manganese and nickel are qualitatively similar to the concentration dependences of the Curie temperature. In both cases, an increase in its values is observed at low concentrations x (figures. 2, 4), and the maximum Curie temperature and magnetic moment of the 3d sublattice is reached at a manganese concentration $x = 0.4$, and at a nickel concentration $x = 0.1$.

To describe the Curie temperature in RCo_2 compounds, it is acceptable to use the following expression [14]:

$$T_C = C_R\left(n_{R\text{-}R} + n_{R\text{-}3d}^2\chi_d\right) = N\frac{g^2\mu_B^2 J_R(J_R+1)}{3k_B}\left(n_{R\text{-}R} + n_{R\text{-}3d}^2\chi_d\right), \quad (2)$$

were: C_R is the Curie constant of rare earth atoms; $n_{R\text{-}R}$ and $n_{R\text{-}3d}$ are the molecular field constants of the intrasublattice $R - R$ and intersublattice R –Co exchange interactions, respectively; χ_d is the exchange- enhanced susceptibility of cobalt sublattice; N is the number of R atoms; J_R is the quantum

number of total angular momentum of rare earth ion; g is the Lande factor; μ_B is the Bohr magneton; k_B is the Boltzmann constant.

Take in account that the spontaneous magnetization of rare earth sublattice is determined by the expression $M_R=Ng\mu_B J_R$. The spontaneous magnetization of 3d - sublattice M_{3d} is induced by the molecular field of rare earth sublattice M_R: $M_{3d}=\chi_d n_{R\text{-}3d} M_R$. The expression (2) can be rewritten as [5]:

$$T_C=\frac{g\mu_B(J_R+1)}{3k_B}(n_{R\text{-}R}M_R+n_{R\text{-}3d}M_{3d}). \quad (3)$$

It is seen from (3) that the Curie temperature of RCo_2 compounds is proportional to the spontaneous magnetization of both rare-earth and 3d- sublattice. We can assume that the increase in the Curie temperature, which is observed with increasing manganese content, is due to the increase in the magnetic moment of cobalt, which may result from changes in the electron structure of the compounds. It is possible, that alloying with Mn and Ni increase the Co magnetic moment due to the additional splitting of the 3d band. This, in turn, leads to an increase in the Tb-Ni (Mn), Co-Ni (Mn) exchange interaction.

The Curie temperature T_C sharply increases to 350 K, and the magnetic moment of the 3d sublattice reaches 1.6 μ_B for the $TbCo_2Mn_{0.4}$ compound. For $TbCo_2Ni_x$ compounds, T_C increases to 233 K, and the magnetic moment of the 3d sublattice reaches 1.38 μ_B at a nickel concentration of $x = 0.025$.

From temperature dependences of magnetization $M(T)$ in magnetic field H_1 = 1 T [11, 12] using well known Maxwell`s thermodynamic relation:

$$\Delta S_m(T, \Delta H)=\int_0^{H_1}\left(\frac{\partial M(T,H)}{\partial T}\right)_H dH\approx\frac{\partial M(T,H_1)}{\partial T}H_1, \quad (4)$$

we determined temperature variation of the magnetic entropy change $\Delta S_m(T)$ in $TbCo_2M'_x$

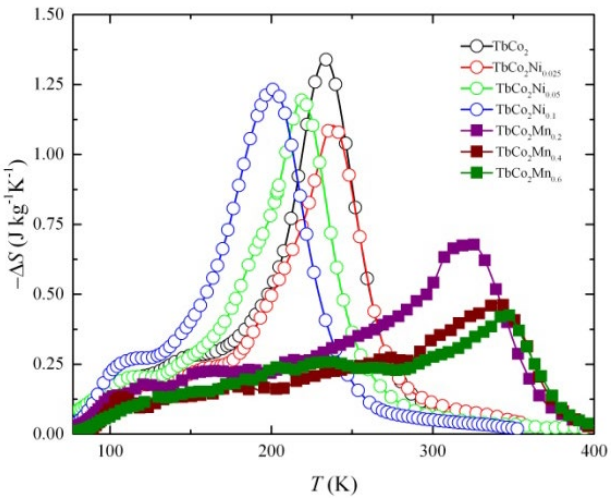

Figure 5. Temperature dependences of entropy change of non-stoichiometric $TbCo_2Ni_x$ $TbCo_2Mn_x$ alloys for magnetic field change $\mu_0\Delta H$ = 1 T.

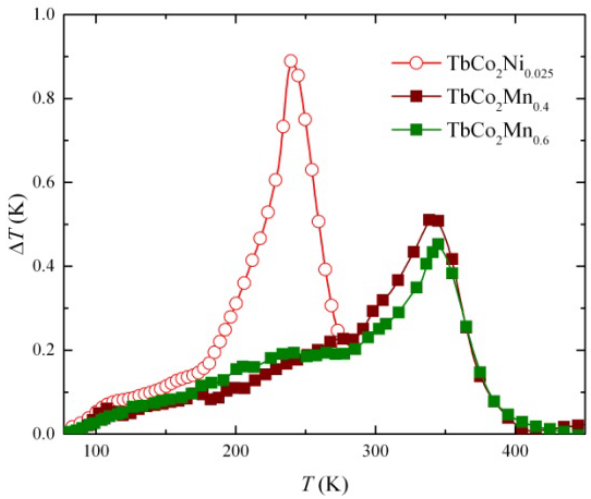

Figure 6. Temperature dependence of adiabatic temperature change for magnetic field change $\mu_0\Delta H$ = 1 T non-stoichiometric $TbCo_2M_x$ alloys.

compounds for magnetic field change $\mu_0\Delta H = H_1 - 0 = 1$ T (figure 5).

For compounds with manganese, there is no pronounced maximum at the Curie temperature, which was previously observed for non-stoichiometric RM_2Mn_x type compounds [4, 5]. On the other hand, the magnetocaloric effect in $TbCo_2Ni_x$ is maximal in a narrow temperature range near the Curie temperature. As can be seen from relation (4), the value of the isothermal change in entropy near the Curie temperature is determined by the rate of change of the magnetization with temperature. With a smooth change of $M(T)$, the $\Delta S_m(T)$ does not change over a wide temperature range.

Absolute values of ΔS_m for $TbCo_2M_x$ decrease with increasing M content because of decreasing the magnetization of alloys. For compounds with Ni, maximum absolute values of ΔS_m is –1.1 $J\cdot kg^{-1}K^-$ for

$\mu_0\Delta H$ = 1 T. For compounds with Mn maximum absolute values of ΔS_m is –0.4 J·kg^{-1}K^{-} for $\mu_0\Delta H$ = 1 T.

The data of the temperature dependence of the heat capacity [11, 12] and the entropy change allow us to calculate the temperature change in a magnetic field using the following expression:

$$\Delta T\,(T)_{\Delta H} = -\frac{T}{C_p(T,\mathrm{H}=0)}\Delta S_m. \quad (5)$$

The maximum value of the adiabatic temperature change for the magnetic field changes from 0 to 1 T is $\Delta T \sim 0.5$ K ($TbCo_2Mn_{0.4}$) and $\Delta T \sim 0.9$ K ($TbCo_2Ni_{0.025}$) (figure 6).

4. Conclusion

Our study showed that single-phase non-stoichiometric $TbCo_2Ni_x$ compounds with $MgCu_2$-type structure exist at a low nickel concentration $x \leq 0.1$. At the same time, single-phase non-stoichiometric $TbCo_2Mn_x$ compounds with $MgCu_2$-type structure exist up to a manganese concentration $x < 0.4$. The concentration range of the existence of the non-stoichiometric $TbCo_2M_x$ compounds with M = Ni is substantially narrower than that for the compounds with M = Mn. This can be because the atomic and ion radii of Ni and Co are less than those of Mn.

The Curie temperature and magnetic moment of 3d sublattice substantially increase for $TbCo_2Mn_x$ and $TbCo_2Ni_x$ compounds as the manganese and nickel content increases. In $TbCo_2Mn_x$, the maximum values of T_C (350 K) and magnetic moment of 3d sublattice μ_{3d} (1.6 μ_B) are reached for $TbCo_2Mn_{0.4}$. For $TbCo_2Ni_x$, the maximum values of T_C (233 K) and μ_{3d} (1.38 μ_B), are reached at a nickel concentration x = 0.025. The analysis of the obtained results shows that an increase in the Curie temperature with increasing concentrations of nickel and manganese is due to an increase in the magnetic moment of the 3d sublattice, which can occur as a result of changes in the electronic structure of compounds.

The magnetocaloric effect at the magnetic field change from 0 to $\mu_0 H$ = 1 T was estimated using magnetic and heat-capacity measurements. For the $TbCo_2Ni_{0.025}$ compound, the maximum magnetic entropy change is –1.1 J·kg^{-1}K^{-1}, which corresponds to temperature change of ~ 0.9 K. For the $TbCo_2Mn_{0.4}$ compound, the maximum magnetic entropy change is –0.4 J·kg^{-1}K^{-1}and the temperature change is ~ 0.5 K.

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